LA-UR-21-25066

Approved for public release; distribution is unlimited.

Title:	Hydrogenous Content in Residues from Aqueous Chloride Pu and Am Recovery Operations
Author(s):	Kimball, David Bryan Rios, Daniel Ahern, John Cory
Intended for:	Internal documentation of operational chemistry and byproducts for the purpose of establishing a technical basis for analysis of byproducts by the Nuclear Criticality Safety Division.
Issued:	2021-05-26

Disclaimer:
Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by Triad National Security, LLC for the National Nuclear Security Administration of U.S. Department of Energy under contract 89233218CNA000001. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

LA-UR-21-XXXXX
Approved for Public Release;
distribution is unlimited.

Hydrogenous Content in Residues from Aqueous Chloride Pu and Am Recovery Operations

David B. Kimball, Ph.D., AMPP-4
Daniel Rios, Ph.D., AMPP-4
John C. Ahern, Ph.D., AMPP-4

May 23, 2021

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by Triad National Security, LLC for the National Nuclear Security Administration of U.S. Department of Energy under contract 89233218CNA000001. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Hydrogenous Content in Residues from Aqueous Chloride Pu and Am Recovery Operations

Abstract

Byproduct residues generated from Aqueous Chloride Pu and Am recovery operations at Los Alamos National Laboratory have been investigated and determined to contain high weight % chloride salts and minimal hydrogen content. Hydrogen content is the result of limited surface area adsorption of ambient moisture. The assumption used in technical analysis NCS-TECH-19-029 to model potentially hydrogenous items as mixtures of polyethylene is shown to be overly conservative. Our results and literature precedent indicate that water adsorption of 1-3 % by weight is expected for hydroxide cakes and Pu oxides, and a conservative bounding assumption for these materials is 5% water by weight. LOH results for a dissolution heel stored long term showed 6.25% weight loss, which was conservatively assumed to be water. A conservative bounding assumption for dissolution heels is 8 wt.% water content. This equates to 0.55 % hydrogen by weight for hydroxide cakes, and 0.88% hydrogen by weight for dissolution heels. The bulk composition of dissolution heels reflects the composition of the original byproduct feed material, chloride salts of potassium, sodium, magnesium and calcium. The bulk composition of calcined hydroxide precipitation residues is composed of potassium chloride as a result of potassium hydroxide neutralization of hydrochloric acid solutions. Metal hydroxides generated during the hydroxide precipitation process are decomposed under the conditions of calcination to metal oxide forms.

Introduction

On July 1st of 2019, the Los Alamos National Laboratory (LANL) Nuclear Criticality Safety Division (NCSD) identified numerous Pu-bearing "hydroxide cakes" in the Plutonium Facility (PF-4) vault. These items were subsequently suspected by NCSD of having significant hydrogen content, and were judged to be "infracted items" without sufficient technical basis through technical analysis NSC-TECH-19-029. Conclusions in NCS-TECH-19-029 were based on the maximally conservative assumption that any excess weight within these items that was not known Pu and/or Am was hydrocarbon polymer, modeled as "a mechanical mixture of plutonium and polyethylene," with high density hydrogen content. Additional conservatisms and treatment of these and similar filter residues ("dissolution heels") as solutions, rather than dry residues, led to restrictions on shelving/removing activities in the vault.

In November of 2020, the NCSD further identified a container in a safe in PF-4 that held an item originating from the Aqueous Chloride (AQCL) Hydroxide Precipitation process. Using similar arguments for residues in the vault, the NCSD called a Potential Process Deviation (PPD) for this item. This event has since been defined as "under review" (NCS-EVENT-20-058) pending characterization of the material constituents of this type of residue. By extent of condition, the NCSD has extended restrictions to several other locations as well.

Hydroxide cakes and dissolution heels represent the two solid byproducts of the AQCL Pu and Am Recovery process (See Figure 1). Dissolution heels are salt residues remaining undissolved after HCl dissolution attempts. Hydroxide cakes are salts precipitated via the Hydroxide Precipitation process on AQCL byproduct acid solutions. AQCL Pu and Am recovery has been used at TA-55 since the 1980s to process byproduct salt residues from Pyrochemical Operations (Molten Salt Extraction, Metal Chlorination, Electrorefining, Direct Oxide Reduction) (1,2). Byproduct salts are dissolved in hydrochloric acid (HCl) so that the majority of the Pu remaining in the feed residues can be separated from the bulk salts and other metal impurities, purified, and calcined into Pu oxide for long term storage and/or conversion back to metal via the Direct Oxide Reduction process. Am is purified separately after separation from Pu, precipitated similarly as the oxalate, and calcined into Am oxide for isotope sales through the DOE Office of Science. Hydroxide Precipitation is used to recover additional remaining Pu/Am from byproduct solutions such that the precipitated solids ("hydroxide cakes") can be further processed or discarded as TRU waste and the spent solutions transferred to the TA-50 Radioactive Liquid Waste Treatment Facility (RLWTF) for further treatment.

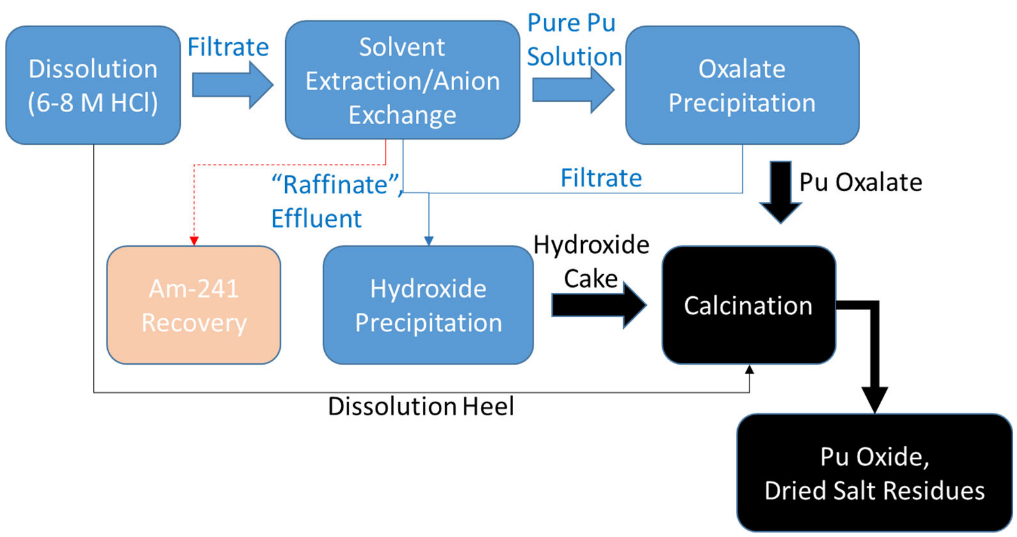

Figure 1. AQCL Process Flow Diagram. Blue represents "wet" operations and solutions, black represents dry operations and solids, and Am-241 recovery is denoted as a dashed line to indicate optional recovery.

The goal of this process is to recover as much Pu and Am as possible from byproduct salts from Pyrochemical Metal Production operations, as well as other chloride containing byproducts and legacy materials (1,2 and see for an example of 2001 throughput reference 3, Supporting Information Tables S1 and S2). Both dissolution heels and hydroxide cakes typically contain only 10s of grams of Special Nuclear Material (SNM: Pu-239, Am-241, etc.). Both residues are calcined/dried, i.e. heated in/on a furnace, after recovery to remove any adsorbed water and to convert any SNM and metal hydroxides to their respective stable oxides.

As a result of AQCL processing, both dissolution heels and hydroxide cakes typically contain minimal quantities of SNM dispersed in a high Cl- containing salt matrix. For example, a survey of AQCL outputs from 2001 showed that for 9 dissolution heels the average SNM content was 1.1 % by wt, and for 64 hydroxide cakes the average SNM was 0.7 % (3, Supporting Information Table S3). For dissolution heels, the bulk of the net weight comes from the Cl^- salt matrix from the Pyrochemical byproduct salt feed (Molten Salt Extraction (MSE), Metal Chlorination (MC), Electrorefining (ER), and to a lesser extent Direct Oxide Reduction (DOR)) (1,2,4). For hydroxide cakes the precipitated salt matrix is the result of salt saturation from the original salt feed along with HCl neutralization using potassium hydroxide (KOH).

Although the chemistry involved in these processes is well known, predictable and supported by numerous literature precedents, and has been used effectively for decades, the recent difficulties bounding potential hydrogen content for nuclear criticality safety purposes (described above) has led operations to more formally characterize AQCL dissolution heel and hydroxide cake residues. The following report details the characterization results obtained for a recently generated hydroxide cake, as well as water content analysis (Loss on Heating, also known as Loss on Drying and Loss on Ignition) of a dissolution heel, as examples from AQCL processing. The results are discussed with regard to the nature of the processes generating these residues, why the results are as expected, and bound the potential hydrogen (due to adsorbed water) content.

RESULTS

CXLCAKE081020 was obtained to characterize hydrogenous constituents of this general type of residue (hydroxide cakes). CXLCAKExxx items are impure solids recovered from the AQCL Hydroxide Precipitation process, after neutralization of HCl feed solutions with KOH solution as described in Section 5.5 of PA-DOP-01421 (5). The resulting precipitates are separated from the solution by filtration and are subsequently calcined in a crucible inside a furnace that is heated stepwise to100 ºC for 2 hours, 250 ºC for 2 hours, and finally to 450 ºC for 4 hours (PA-DOP-01422, Appendix 1, 6). CXLCAKE081020 was calcined per PA-DOP-01422 in August of 2020 and subsequently containerized, removed from the glovebox line ("bagged out" and placed in another container), and analyzed for SNM content. CXLRES081020 is representative of CXLCAKExxx items as it was generated after purification/processing of typical Pyrochemical salt feed items, and following typical neutralization, filtration and calcination processes. The Local Area Network Nuclear Accountability System (LANMAS) element weights for CXLRES081020 are 29.72 g Pu, 4.54 g Am, and total net weight for the item is 734.15 g.

Samples from CXLCAKE081020 were sent to the LANL Chemistry Division, Actinide Analytical Chemistry group (C-AAC) for compositional analysis. The results are given in Table 1.

Although exhaustive elemental analysis was not obtained for CXLCAKE081020, as can be seen from Table 1 this was not warranted (total weight % = 101.46 %, ~10 % uncertainty). We note that we expect that Pu, Am, Fe, and potentially Ca and Mg exist as their stable oxides as the result of calcination operations, and oxygen content was not measured. If Pu, Am, and Fe were to exist as their dioxide and Ca/Mg as their monoxide, this would equate to a minimum oxygen content of ~4.3 % (wt). We also note the low level of hydroxide (OH-) detected (0.0135 % by wt.). This is also consistent with complete calcination to stable oxides.

Table 1: Compositional Analysis of CXLCAKE081020

Cation	**Weight %**	**% Uncertainty**	**Analytical Method**
Potassium	26.9 %	10 %	ICP-AES
Sodium	13.6 %	10 %	ICP-AES
Plutonium	4.05 %	<3 %	Calorimetry/Isotopics
Calcium	2.36 %	10 %	ICP-AES
Magnesium	1.36 %	10 %	ICP-AES
Americium	0.62 %	<3 %	Calorimetry/Isotopics
Iron	0.43 %	3 %	UV-VIS
Total Cations	*49.32 %*		
Anion	**Weight %**	**% Uncertainty**	**Analytical Method**
Chloride	41.9 %	10 %	IC
Fluoride	0.22 %	10 %	IC
Hydroxide (OH-)	0.0135 %	15 % (from average)	Titration
Total Anions	*42.14 %*		

The remaining bulk material in CXLCAKE081020 was split into 4 daughters and Loss on Heating (LOH) was performed on each daughter split. LOH (also known as Loss on Drying or Loss on Ignition (LOI)) is similar to Thermal Gravimetric Analysis in that the material is heated using a specified profile, and mass loss is determined (7). Although chemical composition of what is lost on heating is not determined in LOH experiments, total weight loss can be determined. For the purposes of bounding hydrogen content, mass loss is conservatively assumed to be water. For CXLCAKE081020, the daughter splits were heated to 450 ºC for 20 hours. The results are shown in Table 2.

Table 2. Weight loss of CXLCAKE081020 from LOH at 450 ºC for 20 hours.

Daughter #	Weight Pre-LOH (grams)	Weight Post-LOH (grams)	Weight Loss (grams)	% Weight Loss
1	158.97	156.98	1.99	1.25
2	183.33	181.24	2.09	1.14
3	200.51	198.21	2.30	1.15
4	191.34	189.33	2.01	1.05
			Average =	1.15

Pictures of CXLCAKE081020 were also obtained and are shown in Figure 2. As can be seen, extensive heating left the material largely unchanged.

Figure 2. CXLCAKE081020 (split) before (left) and after (right) LOH at 450 ºC for 20 hours.

We performed similar LOH analysis on a dissolution heel, CXLRES042810, in order to determine potential hydrogen content present as adsorbed water for dissolution heels. CXLRES042810 was recovered in April of 2010 using the AQCL Dissolution and Calcination processes, and stored in the PF-4 vault after nondestructive analysis (NDA) determined SNM content. CXLRES042810 is representative of CXLRESxxx items (residues remaining after dissolution of a feed item originating from Pyrochemical operations). It was filtered during dissolution and subsequently dried in a container on top of a furnace that is heated stepwise to 200 ºC for 3 hours, to 400 ºC for 3 hours, and finally to 650 ºC for 6 hours. A verification of the calcination procedure was done which showed no major changes to the process from PMT2-DOP-CLO-006 that was then superseded by PA-DOP-01422.

A sample was split from CXLRES042810 and LOH performed on the split sample (see Table 3 for details). The 6.27 wt% loss from LOH is conservatively assumed to be water.

Table 3. Weight loss of CXLRES042810 from LOH at 450 ºC for 20 hours.

Material ID	Sample Net Weight Pre-LOH (grams)	Sample Net Wight Post-LOH (grams)	Weight Loss (grams)	% Weight Loss
CXLRES042810	240.85	225.75	15.10	6.27

Discussion

Hydroxide Cakes:

Hydroxide cakes, such as CXLCAKExxx items, are the precipitated result of neutralization of AQCL acidic byproduct solutions with KOH solution. The chemistry is well known and uncomplicated: $HCl + KOH \rightarrow KCl + H_2O$, $M(metal)Cl_n + nKOH \rightarrow M(OH)_n + nKCl$. This process has been used quite effectively and extensively for decades to precipitate most metals, including Pu and Am, as hydroxides, such that neutralized (pH 7-9, bromocresol purple indicator) and filtered waste solutions from the Hydroxide Precipitation process meet the Waste Acceptance Criteria (WAC) for the TA-50 RLWTF.

KCl and NaCl salts will also precipitate, predictably, to the extent governed by several factors including: their concentration, solubility constants (8), final volume after neutralization, and final pH after neutralization. All of these will vary based on the initial salt composition of the feed from Pyrochemical operations as well as volume differences of HCl necessary in AQCL operations from one run to the next. The composition and concentration of metals, both added in Pyrochemical operations such as Mg as well as contaminants such as Fe, will also vary but are the same as the initial feed. No additional contaminants are added throughout AQCL operations, except oxalic acid which is also used to precipitate Pu.

The results in Table 1 for CXLCAKE081020 are as expected: predominantly KCl from neutralization of HCl solutions (up to 8 M) with KOH solution (facility KOH solution = 11 M) as well as the high concentration in the initial feed, and NaCl from the initial feed (to a lesser extent based on the initial feed amount and the higher solubility of NaCl vs. KCl). Neutralization of ~8 M HCl solution (common for Solvent Extraction "raffinate" solution) with 11 M KOH solution alone is enough to give a supersaturated KCl solution (~350 g/L), regardless of additional dissolved salts.

Calcium and magnesium were also obtained in CXLCAKE081020 (Table 1). While Ca is predominantly found in DOR salts, MSE mixtures may contain $CaCl_2$ as a cover salt in addition to $MgCl_2$. Ca and Mg are essentially ubiquitous contaminants in aqueous processing, Ca from the industrial water used to make solutions and Mg from the MgO crucibles used in Pyrochemistry. Both Ca and Mg form sparingly soluble hydroxides in alkaline solutions, which are typically minimized in the hydroxide precipitates through careful control of pH, (9,10) as both are known to give precipitates that are difficult to filter (9). However, the gelatinous Pu hydroxides and Pu oxypolymers are known to entrain other contaminants on precipitation at neutral pH (11).

Regardless, after calcination the Pu, Am, and other contaminants no longer exist as hydroxides (Table 1, Hydroxide (OH-) 0.0135 % by wt.). The AQCL Calcination process drives off waters of hydration and converts metal hydroxides to oxides via heating to above 400 ºC (12-23). This is a well understood process that has been known for quite some time, and for Pu since the 1950s for both hydroxides and oxalates (23). If any oxalic acid is precipitated, either as the acid or as a metal oxalate, it too will be thermally decomposed above 400 ºC (11,19,23,24). Results in Table 1 for hydroxide decomposition are also consistent with previous results obtained by LANL for KOH and NaOH decomposition (25). Figure S4 and S5 show thermogravimetric analysis (TGA) of KOH and NaOH, respectively, heated up to 600 ºC in an argon atmosphere. The TGA spectrum for KOH shows that under these conditions H_2O is released from 200 ºC to slightly above 400 ºC, suggesting complete decomposition of KOH occurs at the latter temperature. Similarly, the TGA spectrum for NaOH shows dehydration starting at around 50 ºC, followed by complete decomposition above 400 ºC. By procedure (as described in PA-DOP-01422 (6) and previous, superseded documents) the hydroxide precipitates are heated to 450 ºC, in a stepwise heating profile described above, for several hours. The purpose of the procedure is to produce a free-flowing powder, devoid of water. The process is repeated until a free-flowing dry powder end state is obtained.

Pu oxide and chloride salts are known to be hygroscopic (see discussion below for dissolution heels), and some adsorption of water on handling is expected as is evident for the 4 daughter splits of CXLCAKE081020. The splits were very similar in total mass (surface area), split in identical conditions (relative humidity), and at the same time. Their LOH results in Table 2 show nearly identical weight loss consistent with recently calcined hydroxide cakes. The results in Table 2 are consistent with the minimum extraneous weight % possible given the % composition of the other elements in CXLCAKE081020 listed Table 1.

<u>Dissolution Heels</u>:

CXLRESxxx items are impure, undissolved chloride salts recovered from the AQCL Dissolution process, and are typically referred to as the dissolution heel as described above. These salts are the solid residue after dissolution of impure feed in concentrated HCl (6-9 M) for several hours (26). The salt residues originate from Pyrochemical operations, and will have a salt/composition based on what process generated the feed, but are predominantly NaCl/KCl (MSE, MC, and ER), $MgCl_2$ (MSE), and $CaCl_2$ (DOR) (1,2,4). Undissolved salts are by definition unchanged by contact with concentrated HCl, with the exception that most of the Pu and Am is removed (3, see Supporting Information Tables S1-S3). Thus, what is recovered from the AQCL Dissolution operation as the dissolution heel will, after calcination, reflect the initial chloride salt composition of the feed. The dissolution heel will not be more hygroscopic than the initial feed, as the remainder material specifically resisted the dissolution process.

Pu as well as most chloride salts are known to be hygroscopic (7,27-30). Adsorption of some water during handling and containerization is expected especially during sampling and analysis. Reports for Pu oxide moisture adsorption have determined that it is a function of "surface area, relative humidity, and time," (27). Mosely and Wing reported that moisture weight % as high as 5% was observed under higher humidity conditions and lower calcination temperatures, however 3% was typical under normal conditions (27). More recently, LANL has reported PuO_2 will not exceed 3% by weight under the conditions experienced by the calcined residues in PF-4 (29). The mass loss from CXLRES042810 of 6.27% is higher than might be expected based on comparison with Pu oxide, however Rammelberg et al. found that Ca and Mg chlorides and oxides hydrate readily at lower temperatures (12). Analogous to Pu oxide, hydration strongly depends on humidity and time of exposure. Thus, the results for this residue are conservatively bounding of hydrogenous (water) content, as it has been processed, handled and packaged as is typical for this type of residue, stored in the vault for over 10 years, and exposed again to ambient moisture during handling/splitting/analysis.

CONCLUSIONS:

Byproduct residues generated by the AQCL Dissolution, Hydroxide Precipitation, and Calcination processes are dried chloride salts with minimal SNM content, and minimal hydrogen content resulting from limited re-adsorption of water. Adsorption of water is a function of surface area, relative humidity on handling, and time. Our results indicate adsorption of water is consistent with slow, surface area adsorption expected from hygroscopic chloride salts and oxides. In the case of hydroxide cakes, calcination per LANL procedure is sufficient to decompose metal hydroxides to oxides. The assumption used in technical analysis NCS-TECH-19-029 to model potentially hydrogenous items as mixtures of polyethylene is shown to be overly conservative. Our results and literature precedent indicate that water adsorption of 1-3 % by weight is expected for hydroxide cakes and Pu oxides, and a conservative bounding assumption for these materials is 5% by weight. LOH results for a dissolution heel stored long term showed 6.25% weight loss, which was conservatively assumed to be water. A conservative bounding assumption for dissolution heels is 8 wt.% water content. This equates to 0.55 % hydrogen by weight for hydroxide cakes, and 0.88% hydrogen by weight for dissolution heels.

ACKNOWLEDGEMENTS

The authors would like to thank Larry Avens, Steve Yarbro, Louis Schulte, and Jacqueline Seay for their reviews and helpful suggestions for this document. We would also like to thank Stephen Willson for coordinating sample analysis, and Laura Worl for her support via the LANL Material Recycle & Recovery Program.

REFERENCES

(1) L. Reichley-Yinger and G. F. Vandergrift, "Recovery of Plutonium and Americium from Chloride Salt Wastes by Solvent Extraction," CONF-871038—13, Proceedings of the Fifth Symposium on SST, October 26-29, 1987, Knoxville, TN.

(2) A. C. Muscatello and J. D. Navratil, "Chloride Anion Exchange Process for DOR and ER Salts," presentation given at the Tenth Annual Actinide Separations Workshop, May 12-16, 1986, Los Alamos, NM.

(3) See Supporting Information, Tables S1-S3. Table S1 shows Vault Feed In and Product Output for AQCL Operations, 2001. Table S2 shows Vault Feed In and Product Output for AQCL Operations, 2001. Table S3 shows Waste Output for AQCL Operations, 2001.

(4) J. D. Navratil, "Process Chemistry of ^{241}Am," *J. Less-Common Metals*, **1986**, *100*, 189-194.

(5) PA-DOP-01421, "Hydroxide Precipitation," Detailed Operating Procedure, Los Alamos National Laboratory.

(6) PA-DOP-01422, "Calcination," Detailed Operating Procedure, Los Alamos National Laboratory. This DOP superseded PMT2-DOP-CLO-006.

(7) D. M. Wayne and J. T. White, "Thermal Analysis and Loss-On-Ignition Techniques," Plutonium Handbook, 2nd Ed., Vol. 6, Ch. 44.6, pp 3167-3200, 2019, D. L. Clark, D. A. Geeson, and R. J Hanrahan eds., American Nuclear Society.

(8) Merck Index, 14th Ed, 2006, Merck & Co, Inc., Whitehouse Station, NJ, pp 1315 and 1481.

(9) D. C. Christensen, D. F. Bowersox, B. J. McKerley, and R. L. Nance, “Wastes from Plutonium Conversion and Scrap Recovery Operations,” LA-11069-MS, 1988, Los Alamos National Laboratory.

(10) L. R. Avens, D. G. Clifton, A. R. Vigil, “Actinide Recovery from Pyrochemical Residues,” Los Alamos National Laboratory publication LA-10281-MS, 1985.

(11) D. L. Clark, S. S Hecker, G. D Jarvinen, M. P. Neu, “Plutonium,” The Chemistry of the Actinide and Transactinide Elements, Ch. 7, L. R. Morss, N. M. Edelstein, and J. Fuger (eds)., Springer, Dordrecht, 2008.

(12) H. U. Rammelberg, T. Schmidt, W. Ruck, “Hydration and Dehydration of Salt Hydrates and Hydroxides for Thermal Energy Storage – Kinetics and Energy Release,” Energy Procedia, 2012, 30, 362-369.

(13) H. Sato, Y. Yamada, N. Ishigure, T. Nakano, H. Enomoto, S. Takahashi, Y. Kubota and J. Inaba, "Retention, Excretion and Translocation of 239Pu in Rats Following Inhalation of 239PuO2 Calcined at 1150 and 400°C," *J. RADIAT. RES.*, vol. 40, p. 197–204, 1999.

(14) A. Irabien, J. R. Viguri, F. Cortabitarte and I. Ortiz, "Thermal Dehydration of Calcium Hydroxide. 2. Surface Area Evolution," Ind. Eng. Chem. Res., vol. 29, pp. 1606-1611, 1990.

(15) T. Yoshida, T. Tanaka, H. Yoshida, T. Funabiki and S. Yoshida, "Study of Dehydration of Magnesium Hydroxide," J. Phys. Chem., vol. 99, pp. 10890-10896, 1995.

(16) S. Music, S. Krehula and S. Popovic, "Thermal decomposition of β-FeOOH," Mater. Lett., vol. 58, p. 444– 448, 2004.

(17) D. Redaoui, F. Sahnoune, M. Heraiz and A. Raghdi, "Mechanism and Kinetic Parameters of the Thermal Decomposition of Gibbsite Al(OH)3 by Thermogravimetric Analysis," Acta Phys, Pol. A, vol. 131, pp. 562-565, 2017.

(18) H. D. Ruan and R. J. Gilkes, "Dehydroxylation of Aluminous Goethite: Unit Cell Dimensions, Crystal Size and Surface Area," Clays Clay Miner., vol. 43, no. 2, pp. 196-211, 1995.

(19) J. E. Narlesky, M. A. Stroud, P. H. Smith, D. M. Wayne, R. E. Mason and L. A. Worl, "LA-UR-12-23790: Characterization of Representative Materials in Support of Safe, Long Term Storage of Surplus Plutonium in DOE-STD-3013 Containers," Los Alamos National Laboratory, Los Alamos, NM, 2012.

(20) P. Ratnasamy and A. J. Leonard, "Structural Evolution of Chromia," J. Phys. Chem. , vol. 76, no. 13, pp. 1838-1843, 1972.

(21) S. Music, M. Maljkovic, S. Popovic and R. Trojko, "Formation of Chromia from Amorphous Chromium Hydroxide," Croat. Chem. Acta, vol. 72, pp. 789-802, 1999.

(22) T. Sato, T. Nakamura and F. Ozawa, "Thermal Decomposition of Nickel Hydroxide," J. Appl. Chem. Biotechnol., vol. 25, pp. 583-590, 1975.

(23) E. F. Westrum, Jr. “The Preparation and Properties of Plutonium Oxides”, The Transuranium Elements NNES, IV-B, edited by Seaborg, Katz, and Manning, 936-945, 1949.

(24) L. J. Crossey, “Thermal Degradation of Aqueous Oxalate Species,” *Geochemica et Cosmochimica Acta*, **1991**, *55*, 1515-1527.

(25) See Supporting Information Figure S4, LANL Thermogravimetric Analysis (TGA) of KOH showing decomposition to K_2O above 400 °C, and Figure S5, LANL TGA spectra for NaOH showing decomposition to Na_2O above 400 °C.

(26) PA-DOP-01418, “Dissolution Using Hydrochloric Acid,” Detailed Operating Procedure, Los Alamos National Laboratory.

(27) J. D. Mosely and R. O. Wing, “Properties of Plutonium Dioxide,” Technical Report by the Dow Chemical Co., Rocky Flats Division, RFP-503, 1965.

(28) M. L. Crowder, J. M. Duffey, R. R. Livingston, J. H. Scogin and P. M. A. Glen F. Kessinger, "Moisture and Surface Area Measurements of Plutonium-Bearing Oxides," J. Alloys Compd., 2009, vol. 488, pp. 565-567.

(29) NMT-15, Pit Disposition Science & Technology, NMT-15:2004-350, 2004.

(30) M. L. Crowder, J. M. Duffey, R. R. Livingston, J. H. Scogin and P. M. A. Glen F. Kessinger, "Moisture and Surface Area Measurements of Plutonium-Bearing Oxides," J. Alloys Compd., vol. 488, pp. 565-567, 2009.

Supporting Information:

Table S1. Vault Feed In and Product Output for AQCL Operations, 2001.

94-1 From Vault

IN	Lot ID	SNM (g)	NET (g)	OUT	Lot ID	SNM (g)	NET (g)
CXLD012901	XBLC8362	231	1820		CXLPROD012901	964	1104.5
	XBLC8362	221	1638				
	XBLC9363	312	2615				
	XBLC9376	239	1890				
	XCAL	6	25				
		1009	7988				
CXLD011801	XBLC8365	249	1630		CXLPROD011801	791	914.2
	XBLC8369	274	1884				
	XBLC9359	252	1555				
		775	5069				
CXLD011001	XBLC6301	222	1875		CXLPROD011001	818	940.6
	XBLC8344	215	1720				
	XBLC5110	217	2065				
	XBLC9347	231	1580				
		885	7240				
CXLD022601	XBLC9382	415	2402		CXLPROD022601	775	890.4
	XBLC9380	208	1210				
	XBCL9349	226	1512				
		849	5124				
CXLD031901	XBCL8357	157	1550		CXLPROD031901	841	969.7
	XBCL6324	169	1165				
	XBCL8339	189	1740				
	XBCL7320	185	1237				
	XBLC7334	192	1117				
		892	6809				
CXLD030501	XBLC9358	216	1338		CXLPROD030501	702	811.2
	XBLC9360	224	1825				
	XBLC9389	312	1263				
		752	4426				
CXLD030601	XBLC9362	215	1600		CXLPROD030601	608	702.9
	XBLC9384	289	1460				
	CAXBL2128A	79	5796.2				
		583	8856.2				
CXLD031901	XBLC8357	156	1550		CXLPROD031901	841	969.7
	XBLC6324	169	1165				
	XBLC8339	189	1740				
	XBLC7320	185	1237				
	XBLC7334	192	1117				
		891	6809				

IN TOTALS	# OF ITEMS	SNM (g)	NET(kg)	OUT # OF ITEMS	SNM (g)	NET(kg)
	31	6636	52.32	8	6340	7.30

Table S2. Pyrochemistry Waste Salt Feed In and Product Output for AQCL Operations, 2001.

Feed From Pyrochemistry

IN	Lot ID	SNM (g)	NET (g)	OUT Lot ID	SNM (g)	NET (g)
CXLD040201	XBS9431	375	1688.4	CXLPROD040201	843	969.3
	XBS9433	447	1948.3			
		822	3636.7			
CXLD032701	XBLC1520	98	1039.8	CXLPROD032701	648	743.3
	XBLC1521	97	1099.3			
	XBS1521	511	1763.1			
		706	3902.2			
CXLD032801	XBS1522	386	2681.7	CXLPROD032801	848	973.3
	XBLC1522	138	2689.5			
	XBS8424	274	1528.4			
	XBLC8424	78	1019.2			
		876	7918.8			
CXLD040501	XBLC1523	26	634.1	CXLPROD040501	696	791
	XBS1523	676	2186			
		702	2820.1			
CXLD042301	XBS8425	287	1565.8	CXLPROD042301	880	1011
	XBS8426	278	1559.5			
	XBLC8425	50	1032.6			
	XBLC8426	70	1083.6			
	XBLC9431	89	1056.4			
	XBLC9433	93	1531.5			
	CXLX040501	2	598.1			
		869	8427.5			
CXLD042601	XBS1520	499	1829.6	CXLPROD042601	840	957
	XBLC1525	83	1200.6			
	XBS1525	232	1498.9			
	CABL2130	22	5184.4			
		836	9713.5			
CXLD051501	XBS9432A	245	1392.9	CXLPROD050201	772	887.6
	XBS9432B	184	1279.2			
	XBLC9432	261	4274.1			
	CAXBL2134	102	5567.2			
	SDXBSOX43S1W2	0	0.3			
	SDXBSOX44S1W2	0	0.7			
	SDXBSOX47S1W	0	0.7			
	SDXBSOX47S2W	0	0.8			
	SSCCXL8	8	3270.9			
	XBSOX380SIBW	0	0.5			
	XBSOX380S1W	0	0.7			
	XBSOX382VDS2W	0	0.2			
	XBSOX382VDS3W	0	0.8			
		800	15789			
CXLD050201	XBS1524	608	1580.3	CXLPROD050201	772	887.6
	XBLC1524	47	1116.9			
	CAXBL2132	47	4070.5			
	CAXBL2133	131	6565.6			
	XBLCXL29	92	6520			
		925	19853.3			
CXLD062601	XBLC1527	78	943.4	CXLPROD062601	865	1018.5
	XBS1527	340	1698.7			
	XBLC1528	131	1297.8			
	XBS1528	182	1819.5			

Table S2, *continued*

	CAXBL1145	73	2248.9				
	CAL-300	7	78				
	CAL-200	5	79				
	CAL-100	2	79				
		818	8244.3				
CXLD062801	XBLC8427	66	902.5		CLXPROD062801	763	875.7
	XBLC8429	66	897.7				
	CAXBL2140	47	2328.1				
	XBS8427	420	1631.1				
	XBS8429	274	1758.6				
		873	7518				
CXLD073001	CXLRES062601	66	603.5		CXLPROD073001	758	869.8
	XBLC1531	16	870.8				
	XBS1531	85	1442.1				
	XBLC8428	132	1303.5				
	XBS8428	442	1637.1				
		741	5857				
CXLD081401	XBLC8432	63	942.3		CXLPROD081401	717	824.9
	XBLC8430	187	1122.7				
	XBS8430	186	1531.1				
	XBS8432	352	1741.9				
	XBS9442	9	1455.6				
		797	6793.6				
CXLD082201	XBLC9435	163	1309.2		CXLPROD082201	566	650.9
	XBS9435	513	1614.5	into	CXLPROD082901		
		676	2923.7				
CXLD082101	XBLC9436	64	810.6		CXLPROD082101	689	792.4
	XBLC9437	55	926.9	into	CXLPROD082901		
	XBS9436	422	1827.5				
	XBS9437	188	1414.9				
		729	4979.9				
CXLD082901	XBLC1529	83	993.3		CXLPROD082901	710	787.8
	XBS1529	591	1887.5	into	***CXLPROD082901***	***1965***	***2231.1***
		674	2880.8				
CXLD091901	CHLSS96	12	4170		CXLPROD091901	905	1033.1
	CXLSS97	9	3930				
	CHLSS98	17	4940				
	CHLSS99	14	4650				
	XBLCCL1601	9	3327.9				
	XBLC1530	99	928.3				
	XBS1530	668	2062.7				
	XBS1533	142	1596.6				
	CAL-10	0	76				
	CAL-0.1	0	78				
		970	25759.5				

FEED IN	**429**	
TOTALS		
# if Items	**SNM (kg)**	**NET (kg)**
86	**12.814**	**137.0179**
PRODS OUT		
TOTALS	**SNM (kg)**	**NET (kg)**
# if Items	**12.272**	**14.0732**
14		

9.84 KG of salts in 47.6 kg er satls in

Table S3. Waste Output for AQCL Operations, 2001.

Hydroxide cakes sent to WMS

Lot ID	SNM (g)	NET (g)
SSCXL1	46	3182.9
SSCXL2	0	2194.9
SSCXL3	4	1.6
SSCXL4	1	472.4
SSCXL5	2	162.5
SSCXL6	4	845.9
SSCXL7	3	1257.2
SSCXL8	5	1102.8
SSCXL9	1	271.9
SSCXL11	4	2429
SSCXL12	7	2937.4
SSCXL13	7	1464.3
SSCXL14	7	500
SSCXL15	15	2356
SSCXL16	2	1023.4
SSCXL17	15	3149.9
SSCXL18	15	2490.4
SSCXL19	2	2075.8
SSCXL21	6	1367.6
SSCXL20	14	974
SSCXL22	25	1476.5
SSCXL23	36	2430
SSCXL24	38	2897.8
SSCXL25	24	2617.3
SSCXL26	28	1668
SSCXL27	26	1668
SSCXL28	8	3380
SSCXL29	12	640.9
SSCXL30	36	3883.1
SSCXL31	18	1150.2
SSCXL32	17	3714
SSCXL33	12	1928.8
SSCXL34	36	2718.2
SSCXL35	16	3749.8
SSCXL36	2	970
SSCXL37	35	3383.6
SSCXL38	4	690
SSCXL39	3	1.5
SSCXL40	4	1495.6
SSCXL41	4	720
SSCXL42	6	1670
SSCXL43	9	1036.1
SSCXL44	9	1.2
SSCXL45	1	604.4
SSCXL46	12	1280
SSCXL47	20	2276.1
SSCXL48	22	2650
TOTAL (1)	623	80961

Hydroxide cakes Cont

Lot ID	SNM (g)	NET (g)
SSCXL49	4	1330
SSCXL50	26	2160
SSCXL51	4	0.9
SSCXL52	4	1820
SSCXL53	2	490
SSCXL54	19	1456.5
SSCXL55	5	2048.2
SSCXL56	1	1331
SSCXL57	1	1067.2
SSCXL58	1	1968.3
SSCXL59	2	1114.7
SSCXL60	1	347.2
SSCXL61	1	1303.6
SSCXL62	16	1759.2
SSCXL63	7	1133.4
SSCXL64	31	1100
TOTAL (2)	125	20430.2
TOTAL	**748**	**101391.2**
# of Items	63	

Residues sent to the WMS

Lot ID	SNM (g)	NET (g)
LSCXL 5	20	1593.2
LSCXL6	23	1509.3
LSCXL7	8	610.6
LSCXL8	28	1655.5
LSCXL9	26	1323.3
LSCXL11	37	3849.4
LSCXL12	7	2010.7
LSCXL13	26	2842.9
LSCXL14	54	6095.4
TOTAL	**229**	**21490.3**
# of Items	9	

SNM (g)	**1077**
NET (KG)	**271.594**
# OF ITEMS	**105**

Figure S4. LANL Thermogravimetric Analysis (TGA) of KOH showing decomposition to K_2O above 400 ºC.

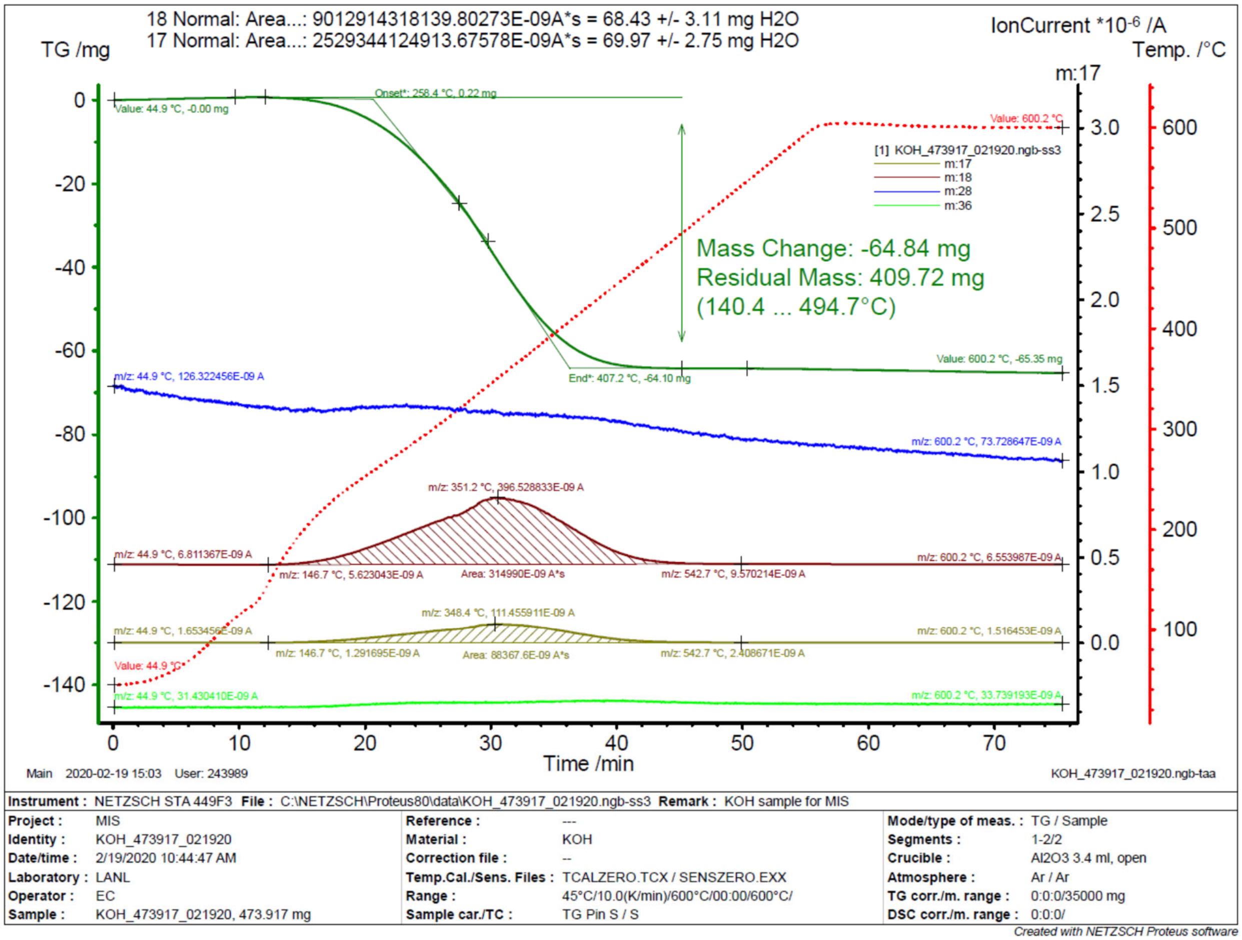

Figure S5. LANL TGA spectra for NaOH showing decomposition to Na_2O above 400 ºC.